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Fluorescent Perylene Diimide Rotaxanes: Spectroscopic Signatures of Wheel–Chromophore Interactions

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Abstract: [2]- and [3]-rotaxanes with a tetraphenoxy perylene diimide core were synthesized. Hydrogen bonding between the wheel and the imide changes the optical properties of the perylene chromophore: the absorption and fluorescence spectra are red-shifted. The decay times of the rotaxanes are shorter in comparison with that of the axle. Single molecule fluorescence measurements reveal relatively narrow distributions of emission maxima and decay times. The averages are in agreement with ensemble measurements. The observed red shifts make the perylene diimide a suitable chromophore for sensing the position of the wheel on the axle.

Keywords: fluorescence spectroscopy · rotaxanes · single-molecule studies · time-resolved spectroscopy · UV/Vis spectroscopy

Introduction

Rotaxanes are supramolecular nanoscale architectures which have recently attracted much attention because of their possible applications as molecular switches and motors.[1–3] Rotaxanes consist of a large ring, the wheel, and an axle, which is threaded through the wheel and kept in place by bulky stoppers at the end of the axle. Controlling the relative position of the wheel with respect to the axle is one of the main challenges for the desired applications. Movement of the wheel can be induced using redox,[4] acid/base[5] or photochemical stimulation.[6] The displacement of the wheel is often monitored using NMR or changes in the optical absorbance spectra. The use of fluorescence for detecting the shuttling process in rotaxanes is less common.[7–12] It is well known in the field of molecular sensors that fluorescence is one of the most sensitive means of detection.[13] Moreover, fluorescence spectroscopy is very suitable for kinetic measurements with high time resolution and high dynamic range. For fluorescence to be useful as a probe for the position of the wheel it is important that interaction between the wheel and the chromophore changes the properties of the latter.

In this paper we describe a [2]rotaxane and a [3]rotaxane with a strongly fluorescent perylene diimide group. In the rotaxanes, the presence of the wheel(s) leads to changes in both the absorption and fluorescence properties of the chromophore. The axle is used as reference compound. Furthermore the (spectro)electrochemical properties of the axle and the rotaxanes are reported. The measurements show that the wheel(s) stabilize(s) the anionic species. Also the fluorescence of individual molecules is studied. These are the first studies of a mechanically interlocked system at the single molecule level.

Results and Discussion

Synthesis: The rotaxanes were prepared using the so-called trapping method (Scheme 1).[14] The 4-tritylphenolate ion forms a complex with the wheel. This complex acts as a supramolecular nucleophile and reacts with the benzylic bromide to form the rotaxane. Because of the presence of

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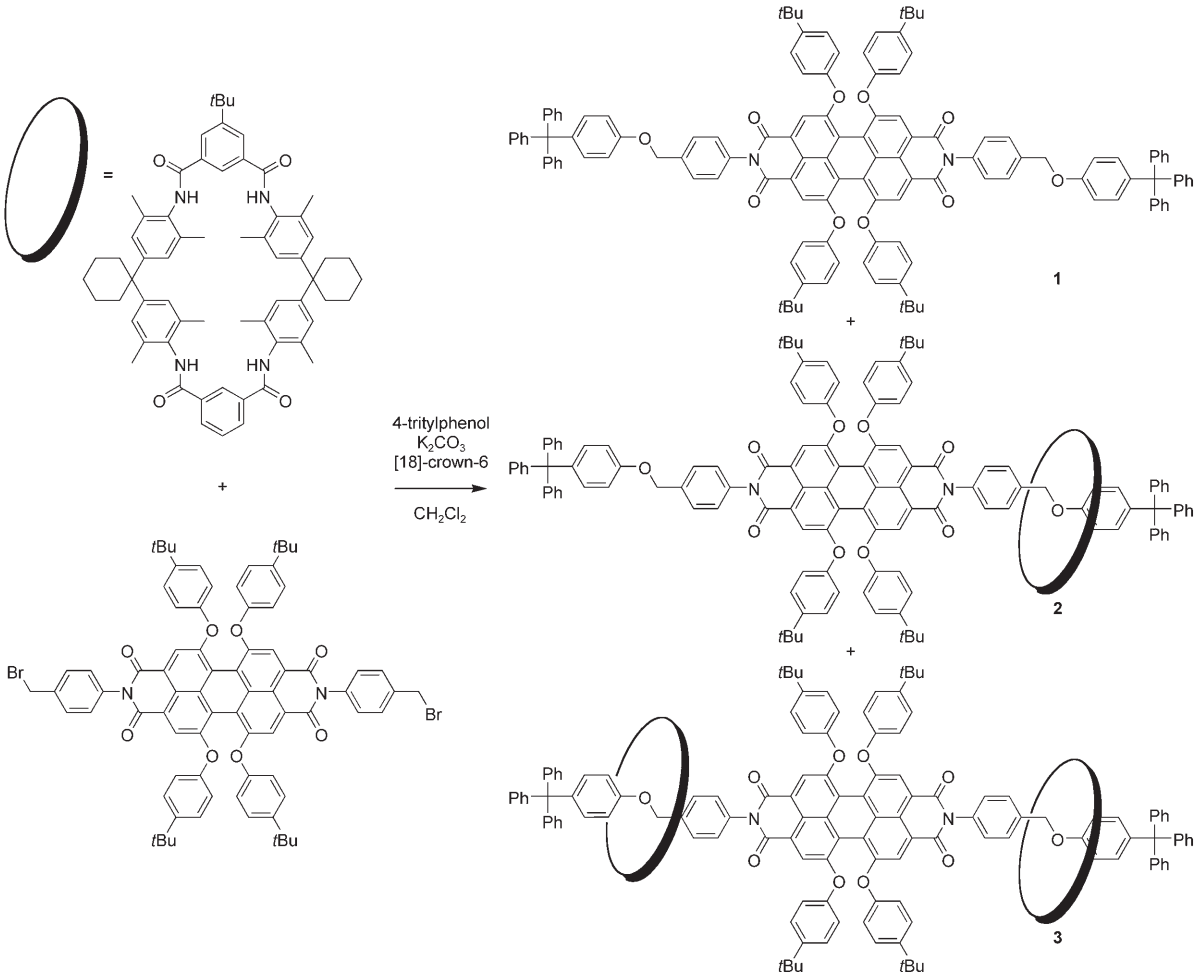
two bromides it is possible to get [2]- and [3]rotaxanes **2** and **3**. If one equivalent of the wheel is used the main product is the [2]rotaxane **2**. The third product is a small fraction of the axle **1**. This is formed by reaction between the uncomplexed phenolate and the benzylic bromide. The three compounds were separated using column chromatography.

Electronic absorption and fluorescence spectra: To study the influence of the wheel on the perylene imide chromophore, absorption and fluorescence spectra were measured in several solvents. The absorption spectra in methylcyclohexane and dimethylsulfoxide (DMSO) are depicted in Figure 1. The fluorescence spectra in methylcyclohexane and DMSO are shown in Figure 2. The data for all solvents used are compiled in Tables 1 and 2. Because of the small amount available of [3]rotaxane **3** this was studied in a limited number of solvents. In methylcyclohexane the axle **1** has its absorption maximum at 570 nm. The maxima of the [2]rotaxane **2** and the [3]rotaxane **3** are red shifted to 593 and 608 nm, respectively. In the fluorescence spectra a similar red shift is observed from 598 nm for the axle **1** to 631 and 648 nm for **2** and **3**, respectively. The observed red shifts are much smaller in DMSO. The maxima of the axle **1**, [2]rotaxane **2** and [3]rotaxane **3** are 577, 580, and 587 nm, respectively, for the absorption and 615, 620, and 624 nm, respectively, for the fluorescence spectra. Also in trifluoroethanol the differences between the spectra of the axle and the rotaxanes are relatively small but now the absorption maxima are around 600 nm and the fluorescence maxima are around 650 nm.

The results show that the excitation energies of the perylene imide chromophore are lower in the rotaxanes **2** and **3** than in the axle **1**. We attribute this to hydrogen bonding between the carbonyl groups of the perylene imide and the amide hydrogens of the wheel. The fact that shifts are seen in the absorption spectra, not only in the emission spectra, demonstrates that the hydrogen bonds exist already in the ground state, in contrast to systems studied previously.[6,7] The shifts of the fluorescence maxima are larger compared with those of the absorption. This indicates stronger hydrogen bonding in the excited state, which is the reason for the red shift of both the absorption and the emission bands.

The Stokes shifts for the axle **1** are small in nonpolar solvents (820–890 cm^{-1}), slightly larger in polar solvents with-



Scheme 1. Synthesis of the rotaxanes studied.

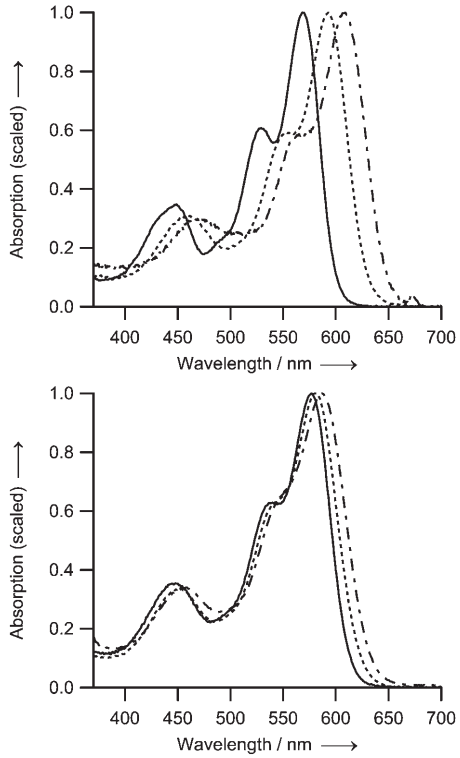


Figure 1. Absorption spectra of the axle **1** (——), [2]rotaxane **2** (-----) and [3]rotaxane **3** (–•–•) in methylcyclohexane (top) and DMSO (bottom). All spectra are scaled to the same maximum absorbance.

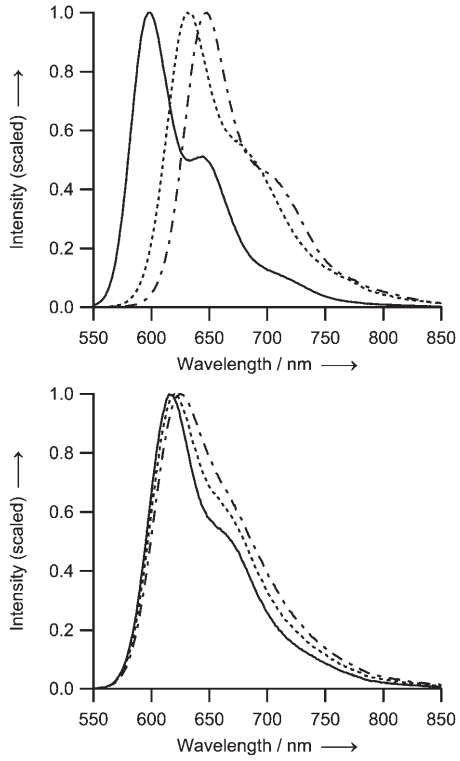


Figure 2. Fluorescence spectra of the axle **1** (——), [2]rotaxane **2** (-----) and [3]rotaxane **3** (–•–•) in methylcyclohexane (top) and DMSO (bottom). All spectra are scaled to the same maximum intensity.

Table 1. Absorption maxima [nm] of axle **1**, [2]rotaxane **2** and [3]rotaxane **3** in different solvents, and shifts induced by the presence of the macrocyclic ring(s) [cm^{-1}].

Solvent	**1**	**2**	**3**	Shift 1[a]	Shift 2[b]
methylcyclohexane	570	593	608	680	1096
toluene	576	598		639	
chloroform	587	602	610	424	642
tetrahydrofuran	568	590		656	
ethanol	578	595		494	
trifluoroethanol	593	609	612	443	523
acetonitrile	570	586		479	
DMSO	577	580	587	90	295

[a] Energy difference between the first absorption maximum of the axle and that of the [2]rotaxane. [b] Energy difference between the first absorption maximum of the axle and that of the [3]rotaxane.

Table 2. Fluorescence maxima [nm] of axle **1**, [2]rotaxane **2** and [3]rotaxane **3** in different solvents, and shifts induced by the presence of the macrocyclic ring(s) [cm^{-1}].

Solvent	**1**	**2**	**3**	Shift 1[a]	Shift 2[b]
methylcyclohexane	598	631	648	875	1290
toluene	607	640	646	849	995
chloroform	622	642	649	501	669
tetrahydrofuran	603	638		910	
ethanol	622	643		525	
trifluoroethanol	645	654	651	213	143
acetonitrile	610	639		744	
DMSO	615	620	624	131	235

[a] Energy difference between the first fluorescence maximum of the axle and that of the [2]rotaxane. [b] Energy difference between the first fluorescence maximum of the axle and that of the [3]rotaxane.

out H-bond donor capabilities (chloroform, tetrahydrofuran, acetonitrile, and DMSO; 960–1150 cm^{-1}) and still larger in hydrogen bonding ethanol (1224 cm^{-1}) and especially trifluoroethanol (1360 cm^{-1}). The solvatochromic effect in the non-specifically interacting solvents is small compared with the effect of hydrogen bond donating solvents. For the [2]rotaxane **2** all Stokes shifts are in the range 1000–1400 cm^{-1}, that is, generally larger than in the axle **1** because in all cases hydrogen bonds are stronger in the excited state. Hydrogen bond donating solvents in this case do not cause especially large shifts, as they do in **1**. Similar spectral shifts were observed in studies of the binding between melamine and perylene imides by Würthner et al.[15,16] They attributed this effect to the polarization of the imide carbonyl groups by hydrogen bonding. In their case the shifts are smaller than in the rotaxanes discussed here.

The effect of the different types of solvent/solute interaction on the absorption and fluorescence maxima can be analyzed using linear solvation energy relationships (LSER).[17,18] One of the most successful proposals for the description of LSER is the Kamlet-Taft expression [Eq. (1)].

$$\tilde{\nu} = \nu_0 + a\alpha + b\beta + s\pi^* \quad (1)$$

The coefficients a, b and s describe the sensitivity of, in this case, the absorption or fluorescence maxima for the differ-

ent solvent properties. The solvent properties are described by the parameters α, β and π^*. The parameter α indicates the hydrogen bond donation ability, the β parameter accounts for the hydrogen bond acceptance ability and π^* is a polarity/polarizability parameter. The observed absorption and fluorescence maxima (in wavenumbers) together with the parameters for the solvents used are shown in Table 3. Fitting the data and the parameters with Equation (1) gives the coefficients in Table 4.

Table 3. Observed absorption and fluorescence maxima in wavenumbers [cm^{-1}] of the axle **1** and [2]rotaxane **2** in different solvents and the solvent parameters[17] for the Kamlet–Taft expression.

Solvent	Axle **1**		[2]Rotaxane **2**		Parameters		
	ν_{abs}	ν_{em}	ν_{abs}	ν_{em}	α	β	π^*
methylcyclohexane	17544	16722	16863	15845	0.00	0.00	0.00
toluene	17361	16474	16722	15625	0.00	0.11	0.54
chloroform	17036	16077	16611	15576	0.44	0.00	0.58
tetrahydrofuran	17606	16584	16949	15674	0.00	0.55	0.58
ethanol	17301	16078	16807	15552	0.83	0.77	0.54
trifluoroethanol	16863	15504	16420	15291	1.51	0.00	0.73
acetonitrile	17544	16393	17065	15649	0.19	0.31	0.75
DMSO	17331	16260	17241	16129	0.00	0.76	1.00

Table 4. Coefficients and standard deviations for the Kamlet–Taft expression obtained by fitting the data in Table 3 to Equation (1).

Coefficient	Axle **1**		[2]Rotaxane **2**	
	Absorption	Fluorescence	Absorption	Fluorescence
ν_0	17530 ± 160	16710 ± 120	16730 ± 130	15680 ± 160
a	−270 ± 130	−540 ± 100	−270 ± 110	−300 ± 140
b	400 ± 250	270 ± 190	460 ± 220	25 ± 260
s	−420 ± 290	−600 ± 220	73 ± 250	26 ± 300
R^2	0.728	0.927	0.799	0.662

In Figure 3 the observed absorption and fluorescence maxima are plotted versus the maxima predicted by Equation (1) using the coefficients obtained by fitting. These plots show the correlation between the experimental data and the model. The correlation is clearly present although the regression coefficients (R^2 in Table 4) are not very large. Only for the fluorescence maxima of the axle **1** a good correlation is found. The obtained coefficients are therefore not very reliable but they can still be used to extract some qualitative information about the influence of the different solvent properties on the absorption and fluorescence spectra.

The coefficient a is negative, indicating that hydrogen bond donating solvents stabilize the excited state. This effect is stronger for fluorescence than for absorption because solvent relaxation is required. This is stronger for the axle **1** than for the [2]rotaxane **2** because in the latter the interaction of the chromophore with the wheel competes with the interaction of the chromophore with the solvent. The positive coefficient b shows that the hydrogen bond accepting solvents have the opposite effect on the spectra: they increase the energy gap between the ground state and the excited state. This effect is larger for the absorption than for the fluorescence maxima. The effect may be due to stabilization of the ground state by electron donating solvents. The effects related to the hydrogen bonding donating and accepting ability are similar for the axle **1** and the [2]rotaxane **2**. This is remarkable because it was expected that hydrogen bond accepting solvents would have a stronger effect in case of the [2]rotaxane **2** due to their tendency to break the interaction between the chromophore and the wheel.

The coefficient s is negative for the axle **1** and slightly positive for the [2]rotaxane **2**. The negative value for the absorption and fluorescence indicate a stabilization of the excited state by polar solvents. In case of the [2]rotaxane **2**, however, this stabilization is absent. This can be explained by a weakening of the hydrogen bonds between the wheel and the perylene imide carbonyl groups in more polar solvents. The weakening of the hydrogen bonds reduces the stabilization of the excited state. The destabilizing effect on the hydrogen bonds is apparently larger than the stabilizing effect of the polarity, which gives a net destabilizing effect.

Electrochemistry: Perylene diimides have beside their strong absorption and high fluorescence quantum yield also useful electrochemical properties. They have high reduction potentials, that is, they are strong electron acceptors. The electrochemical properties of the axle **1** and the rotaxanes **2**

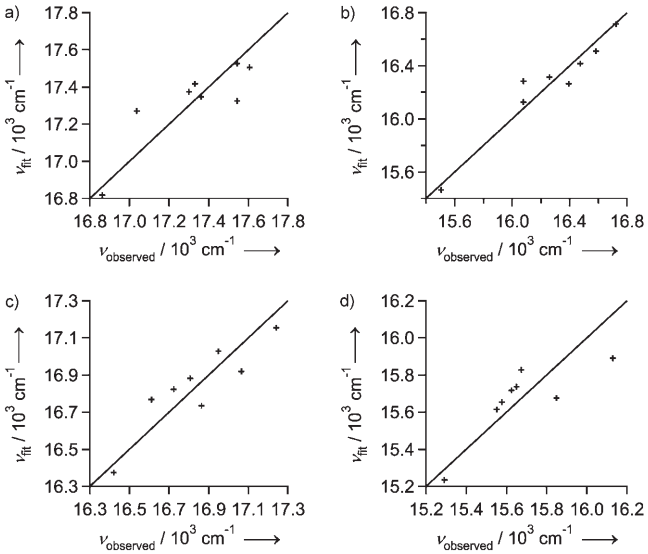


Figure 3. Plots of the maxima obtained from fitting the absorption (a and c) and fluorescence (b and d) maxima of the axle **1** (a and b) and [2]rotaxane **2** (c and d) to the Kamlet-Taft equation versus the observed maxima.

and **3** were determined by means of cyclic voltammetry (Figure 4). The measured redox potentials are summarized in Table 5.

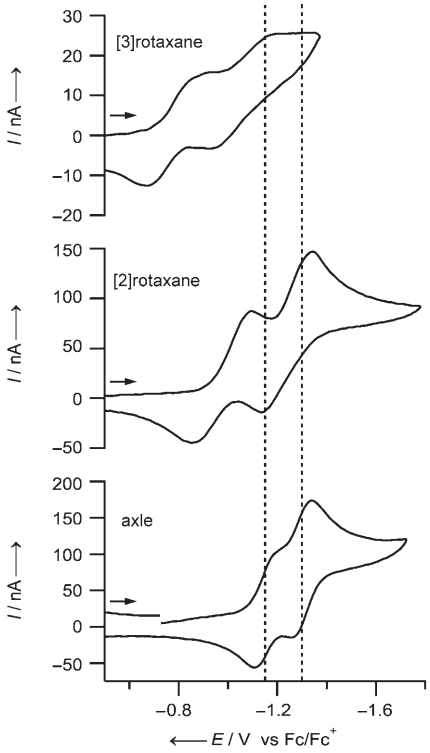


Figure 4. Cyclic voltammograms of the axle **1** and the rotaxanes **2** and **3** in dichloromethane, sweep rate 0.1 Vs^{-1}, concentration ca. 1 mM, supporting electrolyte *n*-Bu_4PF_6.

Table 5. Peak potentials of the reduction and back oxidation of the axle **1** and the rotaxanes **2** and **3** in dichloromethane, and halfwave potentials for the reversible reduction of the axle. All relative to Fc/Fc^+.

Compound	First reduction			Second reduction		
	E_{red} [V]	E_{ox} [V]	$E_{1/2}$ [V]	E_{red} [V]	E_{ox} [V]	$E_{1/2}$ [V]
axle **1**	−1.20	−1.11	−1.15	−1.34	−1.26	−1.30
[2]rotaxane **2**	−1.10	−0.86		−1.34	−1.14	
[3]rotaxane **3**	−0.88	−0.67		−1.18	−0.94	

The halfwave reduction potentials found for the axle **1**, −1.15 and −1.30 V, are similar to the values reported for similar compounds.[15,19,20] The separation between the reduction and oxidation waves is about 80 mV, which is only slightly larger than the theoretically expected 60 mV for a reversible process. The presence of the wheel changes the redox behavior of the perylene core. In the case of the [2]rotaxane **2** the first reduction is shifted to a higher potential, but the second reduction appears almost unchanged. The position of the oxidation wave of the reduced species is, however, changed for both the radical anion and the dianion. The peaks are shifted +0.25 and +0.12 V, respectively. The distance between the corresponding reduction and oxidation waves is much larger than the theoretically expected 60 mV. This indicates that chemical processes are taking place at the timescale of the electrochemical measurement. Probably, these involve conformational changes in which the overall interaction between the wheel and imide increases. The reduction potentials of the [3]rotaxane **3** are affected even more strongly. Now both the first and second reduction are shifted to higher potentials. Also the oxidation of the reduced species is affected more. These effects indicate that the wheels influence the stability of the anions. The fact that the re-oxidation is affected more than the reduction shows that interaction of the wheel with the anions is stronger than with the neutral species. This is also visible in the absorption spectra of the anions (Figure 5).

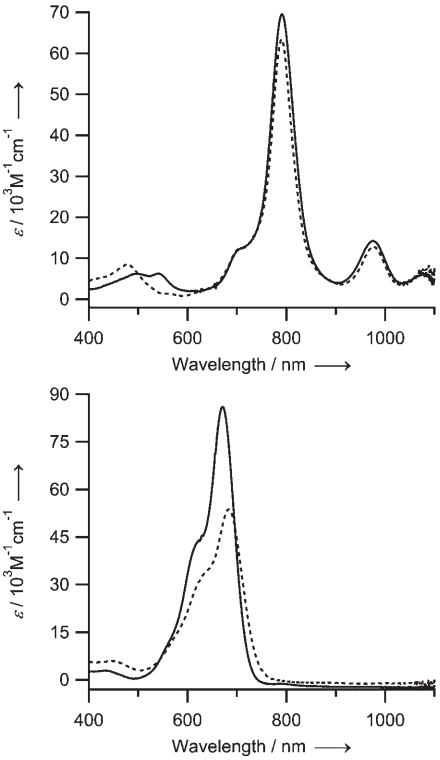


Figure 5. Absorption spectra of the radical anion (top) and the dianion (bottom) of the axle **1** (-----) and [2]rotaxane **2** (——) in dichloromethane.

Only the spectra for the axle **1** and the [2]rotaxane **2** were measured because the amount of [3]rotaxane **3** was too small to obtain good results. The spectrophotometer used could only measure wavelengths between 190 and 1100 nm. This is the reason why the lowest energy absorption band of the radical anion is not completely visible. The spectra of the radical anion and the dianion of the axle **1** and the [2]rotaxane **2** are similar to the spectra observed for similar perylene diimide derivatives.[15,19,20] The absorption maxima and estimated molar absorption coefficients are shown in Table 6. The molar absorption coefficients were estimated using the coefficients measured for the axle **1** and [2]rotaxane **2** in chloroform and assuming full conversion of the

Table 6. Absorption maxima [nm] and estimated molar absorption coefficients [$M^{-1}cm^{-1}$] in parentheses of the neutral species and anions of the axle **1** and the [2]rotaxane **2** in dichloromethane.

Compound	Neutral	Radical anion			Dianion
	λ_{max} (ε)	λ_{max1} (ε)	λ_{max2} (ε)	λ_{max3} (ε)	λ_{max} (ε)
Axle **1**	580 (44×10^3)	1082 (7×10^3)	976 (13×10^3)	790 (63×10^3)	682 (54×10^3)
[2]rotaxane **2**	597 (47×10^3)	1075 (6×10^3)	974 (14×10^3)	791 (69×10^3)	670 (86×10^3)

neutral species to the anions. The absorption spectra of the radical anions of the [2]rotaxane **2** and the axle **1** are almost the same. The maxima that occur at 976 and 1082 nm in the case of axle **1** are slightly blue-shifted in case of the [2]rotaxane **2**. The maximum at 790 nm shows a small red shift. Bigger differences are observed in the range 400–600 nm, but these are partly due to the presence of small amounts of neutral molecules. The blue shift indicates a larger stabilization of the ground state in comparison to the excited state. The extra stabilization of the ground state relative to that of the excited state in the radical anion of the [2]rotaxane **2** is apparently quite small. In the case of the dianion this extra stabilization is larger. The spectrum of the dianion of [2]rotaxane **2** is narrowed and has a higher molar absorption coefficient at the maximum. This might be due a change in the conformation of the perylene core. The stronger binding of the wheel can give rise to some steric repulsion between wheel and the bulky *tert*-butyl phenoxy side chains of the perylene core. This results in a change of the structure and an increase of the oscillator strength. The narrowing of the spectrum might also be caused by the reduction of the number of accessible conformations.

Fluorescence dynamics: Besides the spectral properties, also the excited state decay times can be influenced by hydrogen bonding between the wheel and the (excited) chromophore. To study this, the fluorescence decay times (Table 7) of the axle **1** and the rotaxanes **2** and **3** in toluene, chloroform and DMSO were obtained by single photon counting experiments. The solutions were excited with 614 nm laser pulses and the fluorescence was detected at three different wavelengths: 640, 680, and 720 nm. Identical decay traces were obtained at the three wavelengths, with one exception, discussed below. The decay times for the axle **1** in toluene and chloroform are found to be comparable to those of similar perylene bisimide derivatives.[21,22] In DMSO the decay is faster than in toluene and chloroform, and cannot be described with a single exponential. This behavior is independent of concentration, and is therefore not associated with aggregation.[19] Intramolecular electron transfer between the perylene diimide and the 4-tritylphenoxy stopper group is unlikely to occur on thermodynamic grounds. The reduction potential of the excited chromophore is $E_{red} + eE_{00} = (-1.1 + 2.1)\,V = +1\,V$ versus Fc/Fc^+, which is too low to allow oxidation of a mono-alkoxybenzene unit.[23] It is known, however, that the solvent DMSO can be oxidized by photoexcited C_{60}, which in its T_1 state has a reduction potential of about $+0.8$ V (vs Fc/Fc^+).[24,25] DMSO acts as a sacrificial electron donor,[26] so that a substantial concentration of the C_{60} radical anion can be generated. Irradiation with visible light of axle **1** in argon-saturated DMSO indeed produced the characteristic absorption band of the radical anion at 790 nm. Thus, electron transfer between the photoexcited perylene imide chromophore and the solvent is a quenching pathway for the former. Upon prolonged irradiation, however, other bands were observed as well, which indicates that follow-up or side reactions occur.

Table 7. Fluorescence decay times [ns] and amplitudes (in parentheses) of the axle **1** and the rotaxanes **2** and **3** in some solvents obtained by single photon counting experiments with excitation at 614 nm.

Solvent	Axle **1**		[2]Rotaxane **2**		[3]Rotaxane **3**		
	τ_1 [ns]	τ_2 [ns]	τ_1 [ns]	τ_2 [ns]	τ_1 [ns]	τ_2 [ns]	τ_3 [ns]
toluene	–	6.3	–	6.0	0.9 (0.09)[a]	4.4 (0.91)	–
chloroform	–	6.4	–	6.1	0.9 (0.16)[a]	4.6 (0.84)	
DMSO	1.2 (0.09)	3.6 (0.91)	1.3 (0.58)	3.1 (0.42)	0.2 (0.16)[a]	1.3 (0.48)	2.4 (0.36)

[a] Only observed at 640 nm.

The need to invoke a second exponential term to describe the fluorescence decay can be attributed to conformational heterogeneity. Different orientations of the aryloxy substituents at the bay positions give rise to different conformational species which are likely to have slightly different excitation energies and reduction potentials, which affect the electron transfer rates.

For the [2]rotaxane **2** the decay time is slightly shorter than for the axle **1**. In DMSO, the difference is bigger than in toluene and chloroform, and the short component has gained importance. This can be understood as a result of the increased reduction potential of the perylene chromophore in **2**, which leads to an increased rate and efficiency of electron transfer quenching. It should be realized that this effect is limited by the additional structural reorganization required to form the optimally hydrogen bonded radical anion, as shown above.

The second wheel of the [3]rotaxane **3** has a larger effect on the decay time. In this case the decay times in toluene and chloroform are both substantially shortened. The same is observed for the long lived component in DMSO. In the case of the [3]rotaxane **3** a small contribution from an additional short component can be distinguished at 640 nm. The time constant of this component is 0.9 ns in toluene and 0.2 ns in DMSO, respectively, and may be due to some conformational relaxation in the excited state which leads to red shift of the spectrum in time.[7] A corresponding rise, expected at the long wavelength side of the emission band, could not be resolved.

The fluorescence quantum yield in chloroform was measured using two different references (Table 8). Using the decay times in chloroform (Table 7) and the quantum yields (Table 8) the natural rate constant for fluorescence can be calculated using $k_f^0 = \Phi_f/\tau_f$. The natural rate constant is

$1.4 \times 10^8\ s^{-1}$ for all three compounds. This shows that the lowering of the quantum yield and the shortening of the lifetime are due to an increased rate of nonradiative decay.

Table 8. Fluorescence quantum yields of the axle **1**, and the rotaxanes **2** and **3** in chloroform.

Reference	Axle **1**	[2]Rotaxane **2**	[3]Rotaxane **3**
perylene red ($\Phi = 0.96$)[27]	0.94	0.91	0.63
cresyl violet ($\Phi = 0.54$)[28]	0.88	0.86	0.64
average	0.91	0.88	0.63

A likely reason for the shorter decay times of the rotaxanes **2** and **3** in toluene and chloroform compared with those of the axle **1** is the enhancement of the internal conversion due to the hydrogen bonding between the chromophore and the wheel. If the shortening of the decay time of the rotaxanes **2** and **3** is due to the hydrogen bonding then there could be a correlation between the emission maximum and the decay time: when the rotaxane is in a conformation in which the wheel is not close to the perylene imide the decay time and emission spectrum should be similar to those of the axle **1**. On the other hand when the wheel is hydrogen bonded to the imide the decay time will be shorter and the spectrum red-shifted. Thus, it can be expected that spectral and temporal characteristics will be correlated because they are related to the conformational state of the molecules. Such a correlation between two properties of sub-ensembles cannot be easily determined using bulk experiments, but it can be readily revealed by single molecule fluorescence spectroscopy.[21]

Single molecule spectroscopy: The fluorescence spectra and decay times of individual molecules of the axle **1** and [2]rotaxane **2** in poly(methyl methacrylate) (PMMA) films were measured. The films were spin coated from chloroform. Figure 6 shows the distributions of fluorescence maxima and decay times for the axle **1** and the [2]rotaxane **2**. Here a similar red shift of the fluorescence is observed as in the ensemble measurements. In the case of the axle **1** the occurrence maxima are centered around 580 and 600 nm. For the [2]rotaxane **2** the occurrence maxima are around 600 and 620 nm. The main maximum of the axle **1** at 580 nm shifts to 620 nm in case of the rotaxane **2**. This shift corresponds with observed red shifts in solution. The occurrence maximum at 600 nm is there in both cases. This maximum might be due to hydrogen bonding of some molecules with the polymer (PMMA). This leads to competition between the polymer and the wheel in the case of the [2]rotaxane **2**.

The decay times for both compounds have occurrence maxima around 5.9 ns. This decay time corresponds with the decay time in solution. In case of the axle **1** there is an additional occurrence maximum around 2.9 ns. Such a bimodal distribution of decay times has been found for related perylene imides.[21,22] This was attributed to the presence of different conformers. Apparently, the presence of the wheel makes the conformation with the short decay time less probable. The bulky wheel may have a direct influence on the relative energies of the conformers, which differ in the orientation of the phenoxy groups,[21,22,29] but it is also possible that it prevents the trapping of energetically less favorable conformations in the spin-coated polymer film by creating some local free volume.[30] This leads to the disappearance of the short decay times. For the axle **1**, no correlation between the decay times and the emission maxima was found (see Figure 7). In the case of [2]rotaxane **2** a weak correlation appears to be present, longer decay times being associated with red-shifted emission maxima. This is opposite to what was observed in solution, where red shifts due to hydrogen bonding between wheel and chromophore cause enhanced nonradiative decay. It appears that the restricted dynamics in the polymer matrix suppress this effect.

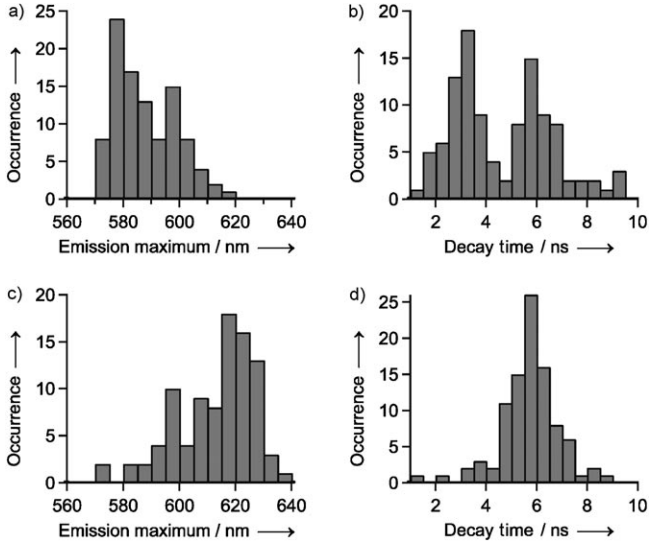


Figure 6. Distributions of fluorescence maxima (a and c) and decay times (b and d) of the axle **1** (a and b) and the [2]rotaxane **2** (c and d) in a PMMA film.

Conclusion

The absorption and fluorescence spectra of the perylene diimide chromophore are red-shifted due to hydrogen bonding between the amide groups in the wheel and the carbonyl groups of the imide. The solvents modulate this effect of the wheel on the spectral properties of the chromophore. The largest spectral shift in going from axle to rotaxane is observed in nonpolar solvents such as methylcyclohexane and the smallest in solvents such as DMSO and trifluoroethanol. In the case of nonpolar solvents hydrogen bonding between the chromophore and the wheel is very favorable, but in DMSO, a strong hydrogen bond acceptor, and trifluoroethanol, a strong hydrogen-bond donor, the red shift is small. This is due to weakening of the hydrogen bonding between the imide and the wheel by competing interactions with the solvent.

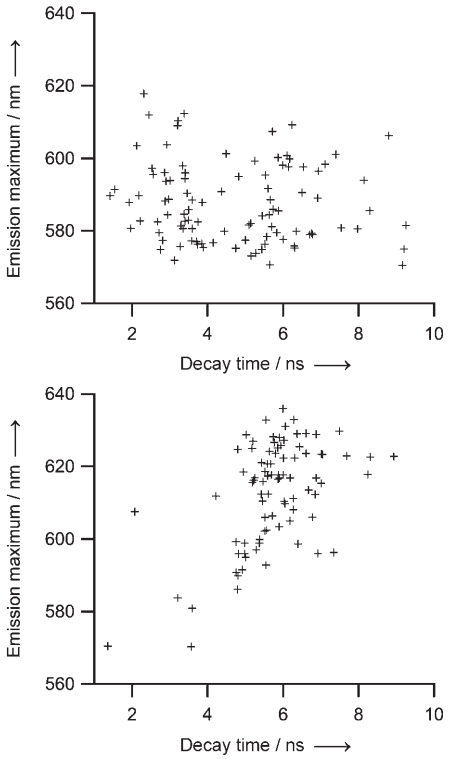


Figure 7. Plots of the emission maxima versus the decay times of the axle **1** (top) and the [2]rotaxane **2** (bottom).

The spectral changes make the perylene diimide a suitable chromophore for reporting the position of the wheel on the axle. The presence of the wheel also gives rise to an increase of the reduction potentials indicating a stabilization of the anionic species by the wheel. This is also visible in the absorption spectra of the anions which shift to the blue. The fluorescence decay times become shorter in the series axle **1** > [2]rotaxane **2** > [3]rotaxane **3**. A similar correlation between the decay times and emission maxima was, however, not found with single molecule spectroscopy of **1** and **2** in PMMA films.

In DMSO, partial quenching of the fluorescence occurs due to electron transfer between the imide and the solvent, which acts as a sacrificial electron donor. The efficiency of this process increases with increasing reduction potential, that it, it is more effective in the series axle **1** < [2]rotaxane **2** < [3]rotaxane **3**.

Experimental Section

Steady-state absorption: Electronic absorption spectra were recorded on two spectrophotometers. The first one is a single beam HP 8453 diode array spectrophotometer with a spectral range from 190 to 1100 nm and a spectral resolution of about 2 nm. The second one is a double beam Varian Cary 3E spectrophotometer, spectral range 190 to 900 nm with spectral bandwidths down to 0.2 nm. The spectra were recorded in rectangular 1 cm quartz cuvettes.

Steady-state fluorescence: Steady-state fluorescence spectra were recorded on a Spex Fluorolog 3 spectrometer, equipped with double grating monochromators in the excitation and emission channels. The excitation light source was a 450 W Xe lamp and the detector a Peltier cooled R636-10 (Hamamatsu) photomultiplier tube. The fluorescence spectra were corrected for the wavelength response of the detection system. The fluorescence of fluorophores in solution was detected in a right angle geometry using solutions with low absorbances (below 0.10). Fluorescence quantum yields were obtained using the comparative method and calculated with Equation (2):[31]

$$\Phi_{\text{sample}} = \Phi_{\text{reference}} \frac{(A_{\text{reference}} I_{\text{sample}} n^2)}{(A_{\text{sample}} I_{\text{reference}} n_0^2)} \quad (2)$$

The subscripts indicate whether the parameter refers to the sample or the reference and the symbols have the following meaning: Φ is the quantum yield, A is the absorption, I is the integrated emission intensity across the band, and n and n_0 are the refractive indices of the solvent of the sample and the reference, respectively.

Time-resolved fluorescence: Time-resolved fluorescence was measured with a time-correlated single-photon counting (TCSPC) setup.[32] This setup consists of a cavity dumped DCM dye laser (Coherent model 700) pumped by a mode-locked Ar^+ laser (Coherent 486 AS Mode Locker, Coherent Innova 200 laser). The fluorescence was collected through a polarizer at the magic angle (54.7°) with respect to the (vertical) polarisation of the laser beam to exclude polarization effects. A microchannel plate (Hamamatsu R3809) was used as the detector. The overall response function (IRF) was measured from the Rayleigh scattering of colloidal silicon dioxide (LUDOX from DuPont).

The fluorescence decay times were obtained from the fluorescence decays by fitting the data with the convolution of the appropriate number of exponentials and the IRF. The fitting was done by numerical iterative reconvolution with a home written program. The program was implemented in Igor Pro 5 and uses a Levenberg–Marquardt algorithm to minimize χ^2.

Single-molecule fluorescence spectroscopy: For this work a confocal fluorescence microscope setup was used at the Katholieke Universiteit Leuven, which is described elsewhere.[33]

Cyclic voltammetry: Cyclic voltammograms were obtained of ≈1 mM solutions of the compound of interest with tetrabutyl ammonium hexafluorophosphate as supporting electrolyte. The measurements were done in gas-tight, single-compartment, three electrode cells equipped with platinum working, coiled platinum wire auxiliary and silver wire pseudoreference electrodes. The cell was connected to a computer controlled PAR model 283 potentiostat. The redox potentials were determined against the ferrocene/ferrocenium redox couple.

Spectroelectrochemistry: UV/Vis spectroelectrochemical measurements were done in optically transparent thin-layer electrochemical (OTTLE) cells with a Pt minigrid working electrode and CaF_2/quartz windows.[34,35] An HP 8453 diode array spectrophotometer was used to measure the spectra.

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